

and poorest parts of the plate is usually from 1·0 to 3·0 parts per thousand, or three or four times as great as that in the case of standard gold. The poorest part in the gold plate is, however, always in the centre and the richest part at the outside.

The assays made on the "get" of the gold plates, the place on the top of the casting where shrinkage of the mass on solidifying is marked externally by a depression, showed that this part was usually richer in gold than any other part of the plate. These assays are not included in the means given above.

Conclusion.

It will be evident from the results given above, that when a small proportion of copper is added to gold, the alloy sets as a whole, and forms a solid solution. If small amounts of copper are successively added, the limit of solubility of that metal in gold is at length reached, and a eutectic separates, which forms the whole mass when about 82 per cent. of gold and 18 per cent. of copper are present.

Comparatively small additions of gold to copper saturate the latter, and the eutectic makes its appearance before the proportion of gold reaches 27 per cent. The composition of the eutectic corresponds approximately to 60 atoms of gold and 40 of copper, while the silver-copper eutectic also contains nearly 60 atoms of silver and 40 of copper. In other respects also, in the brittleness of the eutectic, in the limited mutual solubility of the two metals, and in the liquation which attends solidification, the gold-copper and silver-copper series resemble each other closely. The main difference is that copper appears to be more soluble in gold than in silver, so that the characteristics of the gold-copper alloys are less marked, and consequently have been less easy to detect.

"The Crystalline Structure of Metals." Second Paper. By J. A. EWING, F.R.S., Professor of Mechanism and Applied Mechanics in the University of Cambridge, and WALTER ROSENHAIN, B.A., St. John's College, Cambridge, 1851 Exhibition Research Scholar, Melbourne University. Received May 17,—Read May 31, 1900.

(Abstract.)

The investigations described in this paper deal principally with the phenomena of annealing. The first section of the paper describes experiments made in the hope of observing under the microscope the process of recrystallisation in strained iron. It is well known that

rearrangement of the crystalline structure of iron occurs when the metal is heated to redness, and it is believed that such changes are associated with the evolutions of heat which are indicated by "arrest points" during the cooling of iron. We hoped that by keeping a polished and etched surface of the strained metal under microscopic observation while the specimen was gradually heated, we should see a more or less sudden change in the crystalline pattern at a temperature corresponding to one of the "arrest points." This attempt, however, to watch the process of recrystallisation failed, although the experimental difficulties of keeping a specimen under microscopic observation while it was being heated were successfully overcome. The specimen was electrically heated in a vessel with a thin glass or mica window, and the microscope-objective was kept cool by directing a strong blast of cold air on it and on the surface of the window. In one set of experiments the specimen was kept in an atmosphere of pure hydrogen during the heating, but it was found to become so much tarnished as to obliterate the crystalline pattern. At a red heat, however, the uniform luminous surface of the specimen was seen to develop a number of dark patches which, on slightly raising the temperature, spread over the entire field. No corresponding change was visible during cooling, but the phenomenon would recur every time the specimen was heated, provided it had been cooled below redness after the previous heating. This phenomenon was absent when the specimen was heated in a vacuum, and we believe that it indicates a chemical action between hydrogen and iron, possibly corresponding to the hydrogen arrest point discovered by Sir W. Roberts-Austen.*

In the next series of experiments the specimen was heated in a vacuum. On prolonged heating the specimen still became tarnished, but at first the crystalline pattern remained visible up to a bright red heat. No change in the pattern was observed, but subsequent polishing and etching of the same surface showed that a real change of crystalline structure had occurred. The original etched pattern on the surface had persisted after heating, simply because the differences of level and surface texture on which it depended had in no way been disturbed by the recrystallisation. Any crystalline pattern seen under the microscope, whether it be produced by etching or relief polishing, consists either of coloured surface deposits, or of steps, or pits, or other differences of level in the surface, and these differences of superficial texture, like mechanical scratches, are not affected by rearrangement of the crystalline elements. Coloured surface deposits would also remain unaffected. All attempts to observe the actual process of recrystallisation must therefore be unsuccessful.

The next section of the paper deals with the changes of crystalline structure which go on in lead and other metals at comparatively low

* Alloys Research Committee Report, 'Proc. Inst. Mech. Eng.,' 1899.

temperatures. Our attention was directed to this by noticing that a piece of plumber's sheet lead, when etched with dilute nitric acid, exhibits a strikingly crystalline structure, with large crystals. The character of this appearance led us to the view that a slow process of annealing or recrystallisation was at work in such lead at ordinary atmospheric temperatures, and we have satisfied ourselves that this is the case. The method of investigation consisted in taking a series of micro-photographs, at low magnifications, of certain marked areas in the surface of a specimen, in order to watch the change which went on through lapse of time, or after application of some thermal treatment. It was necessary, for the reasons given above, to re-etch the surface before each photograph was taken.

We have observed that when a piece of cast lead is severely strained by compression, the originally large crystals, after being considerably flattened, are driven into and through one another, so that the etched surface of a strained specimen presents a fine grain, whose crystalline nature only becomes apparent under considerable magnification (80 to 100 diameters). A piece of lead severely strained in this way, and kept for nearly six months in an ordinary room without any special thermal treatment, was found to be undergoing continuous change during that time. A series of photographs of this specimen, taken at intervals during the six months, show that a great number of the small crystals have grown larger at the expense of their neighbours. In similar specimens which have been kept at 200°C. , the growth has been much more rapid and more pronounced. The rate of growth is a function of time and temperature, but some specimens show much more rapid changes than others under similar conditions of temperature; in some cases five minutes' exposure to a temperature of 200°C. is sufficient to alter the crystalline pattern completely. Experiments have also been made at 100°C. and 150°C. , leading to the general result that crystalline growth will occur at any temperature from that of an ordinary room, *i.e.*, 15°C. or 20°C. up to the melting point of lead, and that in general the higher the temperature the more rapid is the initial rate of change. No numerical data can be given, as the crystals are quite irregular, both in size and shape. So far as our observations go, they lead to the result that when such crystalline growth has continued for some time at a given temperature, the structure becomes more or less stable, so far as that temperature is concerned, but exposure to a higher temperature may cause further growth to occur.

A comparison of micro-photographs of the same specimen at various stages reveals the fact that the growth of an individual crystal occurs, not in uniform layers all round it, but by the formation of arms and branches that invade the neighbouring crystals, the intervening portions sometimes changing at a later stage. This action is analogous to the formation of skeleton crystals in a metal during solidification

from the liquid state, the space between the branches filling in as solidification proceeds.

A marked feature observed in several specimens was the large and rapid growth of one or two individual crystals; in several instances such individuals grew until they were some hundreds of times larger than their neighbours. We have not been able to discover the determining cause of such growth nor, in general, why one crystal should grow at the expense of its neighbour. Generally the most aggressive crystals were found near the edges of the specimen. It is noticeable that at times a crystal which has already grown considerably is swallowed up by a more powerful neighbour.

Some light is thrown on the nature of these actions by the fact that this growth only occurs in crystals that have been subjected to severe plastic strain. By casting the metal in a chill mould, specimens of lead can be obtained having a crystalline structure quite as minute as that found in a severely strained specimen, but this structure remains unchanged at temperatures which produce rapid change in a strained specimen.

The investigation of the effects of such comparatively moderate temperatures was extended to other metals, viz., tin, zinc, and cadmium. In tin, the various phenomena of crystallisation from the fluid state are strikingly illustrated on a large scale by the thin layer of that metal which constitutes the surface of commercial tin-plate. The effects of rapid and slow solidification in producing small or large crystals respectively are well marked, and an examination of the etched surface of tin-plate under the microscope reveals beautiful geometrical markings or pits, whose oriented facets produce the well-known selective effect of oblique illumination. The study of the crystalline structure affords an explanation of the nature and method of production of patterns in "*moirée métallique*," a process which has long been in use for the decoration of articles manufactured of tin-plate.

In tin, also, we find that the smallest structure obtainable by quenching the melted metal in water remains unchanged at all temperatures up to the melting point; on the other hand, specimens whose crystalline structure has been modified by great plastic strain exhibit phenomena of recrystallisation at lower temperatures similar to those observed in lead. In a piece of strained tin, an hour's exposure to 150° C. produced complete recrystallisation. Exposure to lower temperatures for this short time produced no visible change, but we have not investigated gradual time effects in this metal. The behaviour of strained zinc and cadmium is analogous to that of tin and lead. Exposure to 200° C. is sufficient to produce rapid recrystallisation in both zinc and cadmium. This is particularly marked in the case of ordinary sheet zinc. On etching commercial sheet zinc, no

large crystals are visible. In this state the metal is strong and tough, bending quite noiselessly. After exposure to 200° C. for half an hour, it shows on etching a large brilliant structure, and the metal is then weak and brittle, and when bent, breaks along well marked cleavage planes and emits a "cry" like that of tin.

In cadmium the recrystallisation is comparatively slow at 200° C., and a time effect has been observed; the action is rather different from that observed in lead. In cadmium the size to which the crystals grow appears to be much more uniform; no arms or branches are thrown out and no twin-lamellæ are found.

The final section of the paper deals with an hypothesis, which is advanced as an attempt to explain the mechanism of the growth of crystals in apparently solid metal.* According to this hypothesis, the metallic impurities which are present in a metal, play an important part in the action. When a metal solidifies from the fluid state, the metallic impurities ultimately crystallise as a film of eutectic alloy in the inter-crystalline junctions; when fairly large quantities of such eutectics are present, the microscope reveals their presence as an inter-crystalline cement, such as that formed by "pearlite" in slowly cooled mild steel; very minute quantities of eutectic, however, will be invisible and yet capable of forming a thin film of fusible cement. We conceive that the changes of crystalline structure which go on while the piece is in the solid state are accomplished by the agency of eutectic films between the crystals, in dissolving metal from the surfaces of some crystals and depositing it on others. When a metal is severely strained, these films of eutectic will be also strained and in many places broken, thus allowing the actual crystals to come into contact with one another. The difference in the rate of etching of adjacent crystals and the phenomena of the electrolytic transfer, in an acid solution, of lead from one crystal to another in the same mass of metal, support the supposition that there is a difference of electric potential between the crystal faces which are brought into contact by severe strain. If it be assumed that a film of eutectic alloy when fluid, or even when in the pasty condition that precedes fusion, can act as an electrolyte, we may regard any two crystals thus in contact, with a film of eutectic interposed in places, as a very low-resistance circuit, and the growth of the positive crystal at the expense of the negative would result. Moreover, such growth would be more rapid at higher temperatures, and its rate at a given temperature would vary in different specimens according to the nature and quantity of the impurities present. That an alloy can act as an electrolyte has not been established experimentally, but the assumption is supported by the close general analogy between alloys and salt solutions. This analogy extends to the very question of the growth of crystals, as

* It is proper to say that this hypothesis is due to Mr. Rosenhain.—J. A. E.

Joly has shown that when crystals of a salt are immersed in their mother-liquor, growth of one at the expense of others will take place.

It should be added that solution of one crystal into the intervening film of eutectic, along with deposit on the neighbouring crystal from the eutectic, may occur as a consequence of differences of orientation, producing differences of "solution pressure" apart from actual electrolysis, but the fact that growth has not been observed to occur except in strained crystals favours the view that the action is electrolytic.

Some further results which have been deduced from the above hypothesis have been verified by experiment. It follows from the hypothesis that an inter-crystalline boundary containing no eutectic would be an impassable barrier to crystalline growth, but if the eutectic could in any way be supplied, growth across the boundary might take place. In an absolutely pure specimen of lead, there would be no eutectic at the inter-crystalline junctions, but as extremely minute traces of impurity would suffice to set up the action, it is almost hopeless to verify the hypothesis in this way. Some experiments on the cold welding of lead have, however, borne out our conclusions. Two clean, freshly scraped lead surfaces will unite under great pressure in the cold state, and if a piece so welded be annealed, we find that the crystalline growth due to the annealing, with very rare exceptions, never crosses the inter-crystalline boundary formed by the welding surface. To test whether the presence of some eutectic would allow growth to take place, we have scattered small quantities of a more fusible metal over the freshly scraped surfaces of lead before squeezing them together. Then, after a cold weld had been made by pressure, on annealing by exposure to 200° C. it was found that crystal growths frequently crossed the line of the weld, as the above theory led us to expect. This experiment has been repeated many times with the uniform result that whenever a small quantity of eutectic, or of an impurity capable of forming a eutectic with the lead, was scattered over the clean surfaces before welding, a distinct growth of crystals across the boundary took place as a result of annealing. On the other hand, a large number of welds were made without introducing any impurity, and with very rare exceptions they showed no growth across the boundary, even after the annealing process was continued for some weeks. In rare exceptions a minute amount of growth across the boundary was observed, but these may fairly be accounted for by the almost unavoidable presence of traces of impurity. The result as a whole goes far to confirm this solution theory of crystalline growth in annealing.